EPA

European Phosphonates

Association

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European Phosphonates Association - input to the revision of the EU Ecolabels related to detergents

Topic 1: Eutrophication

Eutrophication is a synonym for oversaturation with nutrients in the environment. Eutrophication may occur if surface waters receive too much nutrients (e.g. phosphorus, nitrogen, BOD sources), either from sewage works, animal manures, agricultural fertiliser run-off or other sources.

Under ordinary environmental conditions the **only phosphorus source being a nutrient is ortho-phosphate**. Any other type of phosphorus containing substances, whether inorganic or organic, needs to be degraded to form ortho-phosphate to act as nutrition source. Therefore, any readily (bio)degradable phosphorus containing substances will contribute faster and more to ortho-phosphate production than phosphonates.

Phosphonates are completely different substances from the phosphates[1] which were used in the past[2] in Europe before the introduction of phosphate free consumer detergents, and which were accused of contributing to eutrophication in situations where sewage collection and treatment with nutrient removal were not adequately installed.

The phosphorus (P) in phosphonates is not relevant to eutrophication:

- To be effective, phosphonates are needed in detergents at doses which are an order of magnitude lower than for phosphates, which is why the P-limits in the EU Detergent Regulation effectively "ban" phosphates, whilst allowing the continuing use of phosphonates as necessary.
- Phosphonates from detergents are a very minor contribution to total phosphorus in sewage. Less than 1% of total sewage phosphorus taking into account other sources such as food wastes, water treatment, background and surface runoff, food industries etc.
- In sewage works[3], 80 – 97% of phosphonates are removed from water to the sewage sludge[4]. Tertiary treatment (or P-stripping) is not necessary for phosphonates to be removed[5], they are mainly removed in the biological process of treating organic matter in the sewage. Any phosphonates reaching surface waters will tend to adsorb to sediments.

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[1] The phosphate used in consumer detergents was usually the inorganic sodium tripolyphosphate STPP

[2] Phosphates were effectively banned in the EU in domestic laundry detergents from 30/6/2013 and in domestic dishwasher detergents from 1/1/2017 by the imposition of phosphorus limits in the EU Detergent Regulation 259/2012.

[3] This figure is for secondary biological sewage treatment. Even in sewage works operating only "primary treatment" (settling without treatment) over 50% of phosphonates are removed

[4] See HERA Report "Human & Environmental Risk Assessment on ingredients of European household cleaning products: Phosphonates" http://www.heraproject.com/files/30-F-04-%20HERA%20Phosphonates%20Full%20web%20wd.pdf – Nowack, Water Research 36, p 4636-4642, 2002, in tests in real sewage works, found 95% removal after secondary (standard biological) treatment, and 97% after iron-dosing (nutrient removal)

[5] Either biological or chemical nutrient removal will result in even higher phosphonates removal rates

Topic 2: Biodegradability

The most relevant phosphonic acids applied in detergents are HEDP (CAS 2809-21-4), DTPMP (CAS 15827-60-8), ATMP (CAS 6419-19-8), EDTMP (CAS 1429-50-1) and PBTC (CAS 37971-36-1). In context with REACH (European Chemical Regulation) all these structures have been carefully examined with respect to their biodegradability. **None of them is considered to be readily biodegradable**. Typical biodegradation values according to the appropriate OECD methods are below 10 % within 28 days.

The phosphonates used in detergents are not readily biodegradable[6], however a number of studies[7] have shown that **they do biodegrade slowly** in both river water (2), river sediment (3) and in soil (1, 2). This is confirmed by the fact that a number of bacteria, yeasts and fungi have been shown to be capable of breaking down phosphonates to use the carbon and phosphorus they contain (5). This tends to occur in natural systems, where phosphorus is scarce (the micro-organisms break down the phosphonates in order to liberate and metabolise the contained phosphorus), but not in laboratory biodegradation tests which usually use a phosphate-rich medium to sustain microorganism development.

Detergent phosphonates, in the form of metal complexes, which will generally be the case in nature and in sewage, are also broken down by a number of **abiotic mechanisms**:

- **light** (photodegradation) with a half-life of 5 – 23 day[8], which will be the principal breakdown pathway in water and topsoil
- **oxidation** catalysed by natural minerals and micro-nutrients, e.g.: copper, manganese[9] or iron, which will be common in the environment[10]
- **free radical ions**, which occur in soils, in particular in the presence of organic materials

Because **phosphonates do not bio-accumulate and have no chronic toxicity and no aquatic toxicity issues**, this slow biodegradation does not result in risks, as shown by the assessments carried out under the HERA[11] programme and under REACH.

There is no readily biodegradable phosphonic acid on market that has the unique functional properties of phosphonic acids that are essential for their application in detergents (hardness stabilization, sequestration of a various number of metal ions, dispersion and corrosion protection). The readily biodegradable criterion is not relevant here, since there are no toxicity or eco-toxicity issues for phosphonates used in detergent. In fact they are also used for medical applications and in drinking water processes. We also would like to emphasize that phosphonate is allowed in the Nordic Ecolabel (Svanen: R14 part about phosphonates/phosphonic acid in "Dishwashing detergents for professional use" and in 1.2-O7 from the Dishwashing Detergents document).

A ban of not readily biodegradable phosphonates for Ecolabel detergents would mean a loss of a complete category of raw materials.

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[6] *'Readily biodegradable" means 60 or 70% degradability in 28 days in conditions under OECD 301 A-F (intended to simulate a sewage works).*

[7] *(1, 2, 3, 5): Saeger et al. 1977, 1978, 1979, and undated, see REACH dossiers*

[8] *Phosphonates and their degradation by microorganisms, S. Kononova, M Nesmeyanova, Biochemistry (Moscow), vol. 67, n°2, pp 184-195*

[9] *Manganese-catalyzed degradation of phosphonic acids, Nowack et al., Environ Chem Lett, 1, pp. 24-31, 2003*

[10] *Environmental risk assessment of phosphonates, used in domestic laundry and cleaning agents in the Netherlands, J. Jaworska et al., Chemosphere 47, pp 655-665, 2002*

[11] *HERA 2004 http://www.heraproject.com/files/30-F-04-%20HERA%20Phosphonates%20Full%20web%20wd.pdf*

Topic 3: Benefits of allowing the use of phosphonates.

Phosphonates are highly effective components of modern laundry and dishwasher detergent formulations. They contribute to **achieving cleaning performance and hygiene with ecological wash programmes**: lower temperatures and less intensive wash cycles, reducing energy consumption, water use and detergent doses. In phosphate-free laundry and dishwasher detergents, phosphonates are particularly important to ensure this eco-performance.

Phosphonates also protect washing machines/dishwashers, keeping equipment (e.g. heating elements, pipes, nozzles, valves) clean and free from mineral deposits, so improving **appliance eco-efficiency and lifetime**. As they are important in the formulation of concentrated detergents they also have a **positive ecological impact** through **reduced CO2 emissions** for transportation and **reduced amount of packaging and plastic**.

Phosphonates **combine different functions in one molecule**, providing **all-in-one effectiveness at low concentrations**. This is important in detergent formulation, because if a number of different chemicals have to be employed to ensure these different functions, then not only is this more complex and expensive, but it also leads to inefficiencies (as different chemicals interfere with one another), loss of performance reliability (different chemicals may not be stable together) and results in an **increased total detergent chemical load** (several chemicals instead of just one).

Phosphonates stability ensures reliable effectiveness at both low and high temperatures, and under varying chemical, pH or bleach conditions, thus ensuring that they remain efficient throughout the wash process, whatever wash programme is selected. Phosphonates thus facilitate detergent performance in "economy" low-temperature washes and deposit avoidance in low-water consumption programmes and when reduced water volumes are used in rinse cycles.

Additionally, it is well known that the **dispersion capacity of soils will be significantly reduced** without phosphonates. To balance this lack of dispersing power a larger amount of chemicals (cleaning product) will be needed. We believe that this is not a sustainable solution.

Phosphonates are also used as stabilizers for bleaching agents such as hydrogen peroxide and peracetic acid. If phosphonates are not allowed to be used as stabilizer in bleaching boosters the amount of hydrogen peroxide and peracetic acid has to be significantly increased in order to absorb the "normal" degradation. The alternative stabilizer could be phosphate which is being phased out. **Banning the use of non-readily biodegradable phosphonates will lead to an eradication of the use of bleaching agents, which are utmost important in laundry processes.**

EPA (the European Phosphonate Association) is a Sector Group of Cefic, the European Chemical Industry Council.

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